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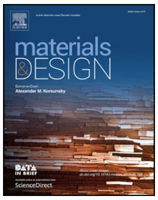

Development and optimization of renewable vinyl plastisol/wood flour composites exposed to ultraviolet radiation

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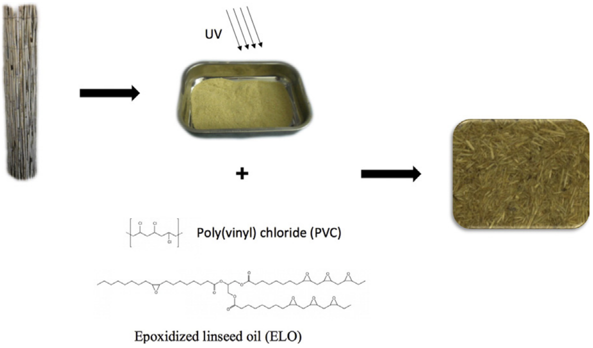
HIGHLIGHTS

- Renewable vinyl plastisol composites based on epoxidized linseed oil (ELO) were developed by introducing reed wood flour
- Optimal materials were observed for vinyl plastisol composites containing 20 to 30 wt.-% of wood flour particles of 500 μm
- Wood flour was exposed to ultraviolet (UV) radiation to increase its interfacial adhesion with the vinyl plastisol
- Ductility of the vinyl plastisol composites prepared with UV-exposed wood flour for 4 min increased up to 3.5 times.

GRAPHICAL ABSTRACT



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ABSTRACT

The application of vegetable oils as novel plasticizers for poly(vinyl chloride) (PVC) is currently in the spotlight of the polymer industry due to their ingrained sustainability. In this study, novel vinyl plastisol/wood flour composites based on epoxidized linseed oil (ELO) were evaluated. For this, PVC was first plasticized by 70 parts by weight of ELO per hundred parts of resin (phr) to form a vinyl plastisol. Wood flour, obtained by dry grinding from reed (*Phragmite communis*), was then incorporated at five different loadings (10, 15, 20, 25, and 30 wt.-%) and three particle sizes (100, 250, and 500 μm). The effect of ultraviolet (UV) radiation was explored to activate the surface of wood flour to increase its interfacial adhesion with the vinyl plastisol. Stereomicroscopy and scanning electron microscopy (SEM) were used to examine the composites fracture and determine the dispersion of wood flour in the vinyl matrix. As per the surface appearance and mechanical results, optimal materials were observed for vinyl plastisol composites at high contents of wood flour with the largest particles that were previously exposed to UV for 4 min. Resultant renewable vinyl plastisol composites show a great deal of potential as designed materials for wood replacement in building applications.

1. Introduction

Plasticizers are well-known additives employed to increase flexibility of thermoplastic materials that can facilitate processing by reducing the melt viscosity and lowering the glass transition temperature (T_g) [1]. The major demand for plasticizers can be found in a multitude of vinyl plastics, which are manufactured by the full spectrum of compounding and fabrication processes employed in the plastics industry. Dissimilar amounts of plasticizers are typically applied to make poly(vinyl chloride) (PVC) workable for a wide range of applications, such as building and construction, packaging, automotive, electrical and electronics, toys, agriculture, furniture, stationery, household, *etc.* [2]. The combination of a PVC resin with a large fraction of plasticizer

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forms a PVC paste or viscous liquid, called "vinyl plastisol", in which the plasticizer component in the formulation generously exceeds 50 wt.-% [3].

Vinyl plastisols are liquid suspensions of fine PVC particles and aggregates highly dispersed in the plasticizer media with other additives. In commercial practice, these typically undergo solidification by controlled heating in a chamber (*e.g.*, an oven) at about 140–180 °C [4]. Since the plasticizer molecules are intimately associated with the PVC particles, the final properties of the plastisol significantly depend on the curing conditions, *i.e.*, temperature and time [5]. As the plastisol is heated, the plasticizer starts diffusing into the PVC particles, solvating their non-crystalline regions, swelling the individual particles, and causing an intense rise in the paste viscosity [6]. With continued heating, solvation of crystalline parts of PVC drops the paste viscosity, allowing polymer molecules to flow more freely [7]. Typically it is necessary to reach temperatures above 190 °C to produce complete fusion of PVC microcrystallites to form a homogeneous matrix with absorbed plasticizer [8]. Once cooled, the plastisol acquires the gel structure and it becomes a solid material with very high particle cohesion and certain flexibility [9,10].

Among PVC plasticizers, general-purpose phthalate plasticizers have historically served as the preferred choice as they provide a desirable balance of cost *vs.* performance. However, these are usually not chemically bonded to the PVC matrix so that they can migrate while being used or after disposal [11]. This has risen considerable concerns, as some studies suggested that phthalate plasticizers for PVC can potentially bioconcentrate and/or bioaccumulate in some species of fish and amphibians, acting as carcinogenic and endocrine disruptors [12]. This has addressed the vinyl industry to produce alternative bio-based and nontoxic plasticizers, which can be still capable of achieving similar performance to that of traditional phthalate plasticizers [13,14].

Vegetable oils have attracted considerable attention in recent years as novel alternatives to phthalate plasticizers for PVC due to their low ecotoxicity, total or partial biodegradability, ready availability in large quantity, and competitive cost [15–17]. These naturally occurring additives are derived from plants and predominantly consist of triglycerides, *i.e.*, the glycerol esters of fatty acids [18]. The amount and nature of fatty acids vary within different oils and even within the same plant oil that is, in turn, dependent on the plant species and, seasonally, on the growing conditions [19]. This determines the degree of unsaturation of the fatty acid, *i.e.*, the number of double bonds, which is measured by the iodine value (IV) and it plays a significant role in the physico-chemical properties of the oil. In this sense, linseed oil extracted from oilseed flax (*Linum usitatissimum* L.) presents a relatively high IV, typically in the range of 168–204, by which it is catalogued as a drying oil ($IV > 130$) [20]. Such rich linolenic content, *i.e.*, *ca.* 55% [21], makes linseed oil a good candidate for bio-based thermosetting polymers application in which high cross-link densities are preferred [22].

As the internal double bonds present in the fatty acids of linseed oil are relatively rich in electrons, they are susceptible to epoxidation process by which both carbons of the double bond become linked to an oxygen atom. Epoxidized linseed oil (ELO) is commonly prepared in the industry using peracids such as performic and peracetic acid [23]. ELO, together with epoxidized soybean oil (ESO), accounts for an annual industrial production >200,000 tons [24]. Similar to ESO, ELO holds many outstanding properties such as good lubricity, low volatility, low odor, and good solvency for being applied in the vinyl industry. However, ELO offers lower migration profiles for PVC than ESO due to its higher molecular weight (MW) and its remarkably higher oxirane oxygen content (OOC), *i.e.*, *ca.* 8–9%, which leads to more intense interactions [25]. In this sense, some recent studies have showed the potential of ELO as a plasticizer in PVC and vinyl plastisol [25–28]. ELO does not only deliver flexibility due to an internal lubrication effect but also increases the polarity and the stability of PVC [22]. The stabilization effect is due to the presence of epoxide groups, which are capable to scavenge acid groups, resulting in a positive effect on the overall polymer stabilization [29].

Natural fillers can be additionally incorporated to increase the sustainable profile of PVC, resulting in renewable vinyl composites [30]. The incorporation of cellulosic materials is justified not only for their neutrality with the environment but also to improve their superficial aspect and reduce cost [31]. Wood flour obtained by conventional grinding is gaining increasing acceptance in vinyl plastics since it offers many advantages, including low density, renewability, high availability, triggered biodegradability, noise absorption, minimum damage during processing, *etc.* [32]. Resultant renewable filled vinyl plastisol composites show potential for wood substitute applications like door shutters, flooring tiles, roofing sheets, partitions, and decking boards [33]. However, these composites can present some important limitations in relation to their mechanical performance as the wood particles habitually present poor compatibility with the vinyl matrix. This effect is produced due to the hydrophilic nature of vegetable fillers, which are mainly composed of cellulose, hemicellulose, and lignin, and their relatively high moisture content, *i.e.*, 8–12.6% [34]. The polar hydroxyl groups on the surface of the cellulosic particles then have difficulty in forming a tightly bonded interface with the nonpolar vinyl matrix. Furthermore, the incorporation of cellulosic fillers in the polymer matrix is often associated with insufficient dispersion, caused by the tendency of the fillers to form internal hydrogen bonds. This leads to some large discontinuities along the polymer matrix that may act as a stress concentrator, the so-called "notch effect", *i.e.*, high concentrations of stress around the fiber perimeter that favors the initiation and spread of cracks. For instance, a brittle-type fracture behavior was reported to PVC composites by Shah et al. [35], who related the low mechanical strength to a low interfacial adhesion between wood flour and the vinyl matrix.

Adhesion properties of polymer matrix-cellulosic filler can be improved by different surface treatments focused on cleaning and/or activating the filler surface in vinyl composite systems. Some smart strategies to increase the fillers interaction capacity include the use of oxidant substances (*e.g.*, chromic and nitric acid, ozone, and hydrogen peroxide), alkali treatments, *i.e.*, mercerization (*e.g.*, NaOH), coupling agents (*e.g.*, silane agents and maleic anhydride-grafted polymers), and physical methods (*e.g.*, electric discharge, plasma, and radiation treatments) [34–40]. The most common radiation treatments comprise ultraviolet (UV), electron beam, and gamma radiation. Compared to the wet process of using chemicals, radiation treatments are able to modify the surface energy without changing the bulk mechanical properties of the fillers [38]. Among them, UV radiation is considered as a straightforward and cost-effective methodology for polymer composites. Kato et al. [39] were the first to oxidize cellulose by UV radiation at vacuum to introduce carbonyl and carboxylic acid groups onto the fillers surface. The efficiency of the UV method was comparable to chromic and nitric acid, whereas it was better than ozone and hydrogen peroxide. More recently, Khan et al. [40] improved the wettability of jute fibers by UV radiation, which increased the composite strength.

The aim of this research work was to optimize the appearance and mechanical performance of ELO-based vinyl plastisol composites with reed wood flour. With the objective to increase their compatibility with the vinyl matrix, the wood flour particles were exposed to UV radiation in a previous stage. The renewable composites were characterized in terms of superficial aspect, mechanical properties, and morphology. Finally, the thermomechanical properties were also evaluated to ascertain their application at room conditions.

2. Experimental

2.1. Materials

Commercial Lacovyl PB 1172 H from Atofina (Midlands, UK) was used as the base resin for the study. This PVC is produced by microsuspension polymerization for the preparation of plastisols. According to the manufacturer, this grade is characterized by a viscosity index of 115 ml/g and kwert (k) value of 67 obtained by ISO 1628-2.